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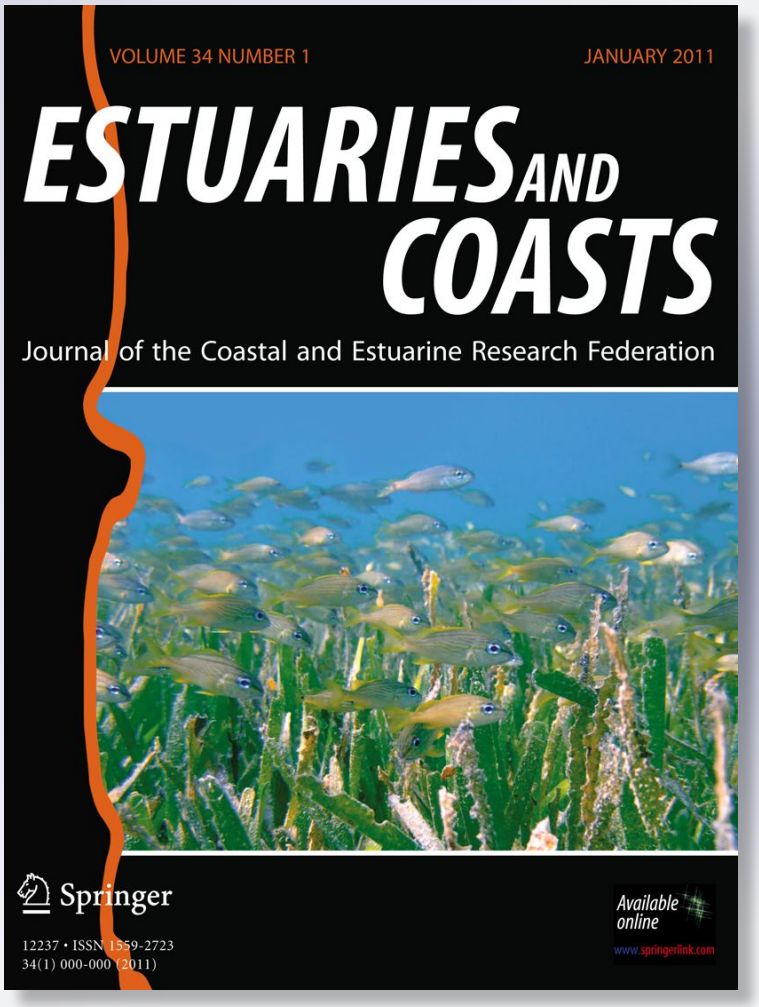
Estuaries and Coasts
Journal of the Coastal and Estuarine Research Federation

ISSN 1559-2723
Volume 34
Number 6

Estuaries and Coasts (2011)
34:1129-1139
DOI 10.1007/s12237-011-9389-3



Springer

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Received: 3 November 2010 / Revised: 10 January 2011 / Accepted: 14 February 2011 / Published online: 1 April 2011

Abstract This paper reports a study of the occurrence and levels of polycyclic aromatic hydrocarbons (PAHs) in a bay characterised by a chronic persistent impact. A total of 55 sediment samples were taken at different depths up to 111 m in two sampling campaigns. Chemical analyses were carried out by gas chromatography-mass spectroscopy. The results indicate that: (1) significant spatial variations exist, (2) levels of PAHs are related more strongly to the spatial distribution of sediments than to mineralogy/granulometry, (3) the sediments are slightly-to-moderately contaminated by PAHs, and (4) these PAHs derive from pyrolytic and petrogenic sources. Through use of an innovative data classification system (proposed according to depth and spatial location of sampling points), and using factorial and cluster techniques, five zones have been differentiated depending on the contamination level and source.

Keywords Spatial classification · Marine · Sediment · Polycyclic aromatic hydrocarbons

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of widespread environmental pollutants containing two or more fused benzene rings. The main sources of PAHs in the aquatic environment include: incomplete combustion at higher temperatures of recent and fossil organic matter (pyrolytic source), slow maturation of organic matter under geochemical gradient conditions (petrogenic sources) and short-term diagenetic degradation of biogenic precursors (diagenesis) (McElroy et al. 1989; Neff 1979). Some of these PAHs are chemicals with known carcinogenic potential (IARC 1983). For example, Giacalone et al. (2004) found that some PAHs can cause liver tumours in several species of fish and other aquatic organisms. Because of these properties and the environmental implications, 7 PAHs are included in the list of Priority Pollutants of the European Water Framework Directive (Council Directive 2008/105/EC 2008) and 16 in the United States Environmental Protection Agency (USEPA) Priority Pollutant List (Code of Federal Regulation 1982).

General trends in the distribution of PAHs can be observed between the two predominant sources: petrogenic and pyrogenic. To differentiate both sources, several indexes are used that include the ratio between low molecular weight (LPAHs) and high molecular weight (HPAHs) PAHs (Soclo et al. 2000). LPAHs (< three rings) are produced abundantly at low-to-moderate temperatures, such as during wood and coal combustion. On the contrary, HPAHs (> four rings) are generated at high temperatures, such as in vehicle emissions (Mastral and Callen 2000). Other frequently used indexes are the phenanthrene/anthracene, fluoranthene/pyrene, and pyrene/benzo[a]pyrene ratios (Macías-Zamora et al. 2002). Due to their low water solubility and their

hydrophobicity, PAHs in the marine environment rapidly become associated with organic and inorganic suspended particles (Chiou et al. 1998) and they are subsequently deposited in sediments. As PAH solubility decreases with increasing molecular weight, bioaccumulation of PAHs from sediments by marine organisms is generally greater for the lower molecular weight and more water-soluble PAHs (Djomo et al. 1996; Porte and Albaigés 1993). PAH levels in marine sediments have a highly heterogenic spatial distribution depending on several characteristics of the studied location, i.e., source, abundance, local atmospheric/marine circulation regimen, etc. For example, PAH concentrations as high as 48,000 ng/g were found in the Venice lagoon (La Rocca et al. 1996); levels between 5,700 and 8,500 ng/g were found in the Mediterranean littoral of France-Spain (Baumard et al. 1999); and levels of approximately 800 ng/g were found in Todos Santos Bay, Mexico (Macías-Zamora et al. 2002).

In this study, the Bay of Algeciras (Spain), a unique and important coastal environment located in South-western Europe at the frontier between the Atlantic Ocean and the Mediterranean Sea, was selected as the sampling area. The Bay suffers from chronic anthropogenic pollution from the urban and industrial activities of the zone (including an important petrochemical industry) and the maritime traffic using Algeciras Harbour (ranked among the most important ports of the world; AAPA 2007). The aim of this study was to describe the zoning of a typical coastal geomorphologic unit (the semi-enclosed bodies of water) according to its sediment pollution. For this purpose, a new spatial distribution methodology has been proposed in this work, which, together with factorial and cluster analysis, provides an useful tool for studies in marine sediments, allowing the zoning, and consequently the selection, of priority areas. This methodology can be applied in different coastal areas around the world, and to different characteristics of sediments, representing a multidisciplinary tool that is applicable to different studies in the marine environment.

Materials and Methods

Study Area

The Bay of Algeciras is located on the Strait of Gibraltar (Southern Spain) and is delimited by Punta del Carnero (near the city of Algeciras) and Punta Europa (Gibraltar). The bay is 9 km wide and 10 km long, covering an approximate surface area of 70 km^2, with a depth of up to 400 m in the centre of the bay and 460 m in the mouth. This coastal area has suffered the chronic impact from urban and industrial sources for several decades. Five important cities are located around the bay (Fig. 1a): Algeciras, Los Barrios, San Roque, La Línea de la Concepción and Gibraltar. Together, these urban areas have more than 250,000 inhabitants ('agglomeration' according to EU Directive 96/62/CE; Council Directive 96/62/EC 1996).

This bay is also an important industrial area of the Mediterranean Sea, with a large refinery (capable of processing 12 million tons of crude oil annually) and its associated petrochemical industry, in addition to steel, paper and power production (four thermal power plants) (Fig. 1a). Another important source of pollution is the intense maritime traffic associated with the transport of oil to and from the refinery, bunkering activities in the bay, and the commercial shipping activities of the Algeciras Harbour, one of the largest in Europe, which handled 43 million tons of goods in 2007 (APBA 2008).

Sample Collection

In November–December 2006 and October–December 2007, two sampling campaigns were carried out and a total of 55 superficial sediment samples were collected in 36 locations along 10 transects (Fig. 1a). Samples were taken with a Van-Veen grab at depths ranging from 3 to 110 m. From each location, approximately 400 g sediment was placed in amber borosilicate containers with polytetrafluoroethylene (PTFE) tops and stored at −20°C for subsequent analyses. Additionally, an extra 400 g was collected in plastic bags to characterise the sediment (organic matter content, granulometry and mineralogy).

Analytical Procedure for PAHs

PAH analysis was based on the analytical procedure proposed by USEPA (1996, 2000). Approximately 2–4 g sediment was weighed with 0.001 g precision and dehydrated with anhydrous Na_2SO_4. The samples were Soxhlet-extracted with 10 mL dichloromethane-acetone (8:2 v/v) for 24 h (6 cycles per hour). The extracts were purified on florisil columns, and the PAHs were eluted with 100 mL dichloromethane-hexane (2:8 v/v). The extract was concentrated to 1 mL using a rotary evaporator after changing the solvent from dichloromethane-hexane to acetonitrile. Na_2SO_4 was of analytical grade and dichloromethane, hexane, acetone and acetonitrile were HPLC grade.

The composition and concentration of 16 different PAHs were determined by gas chromatography-mass selective detection (GC-MSD) using a Voyager (ThermoElectron; http://www.thermofisher.com) gas chromatograph according to a modified version of the method described by Anyakora et al. (2005). The instrument is equipped with a split/splitless injector and a splitless time of 1 min was used. The injection volume was 1 µl. The injector temperature was maintained at 250°C. The GC temperature

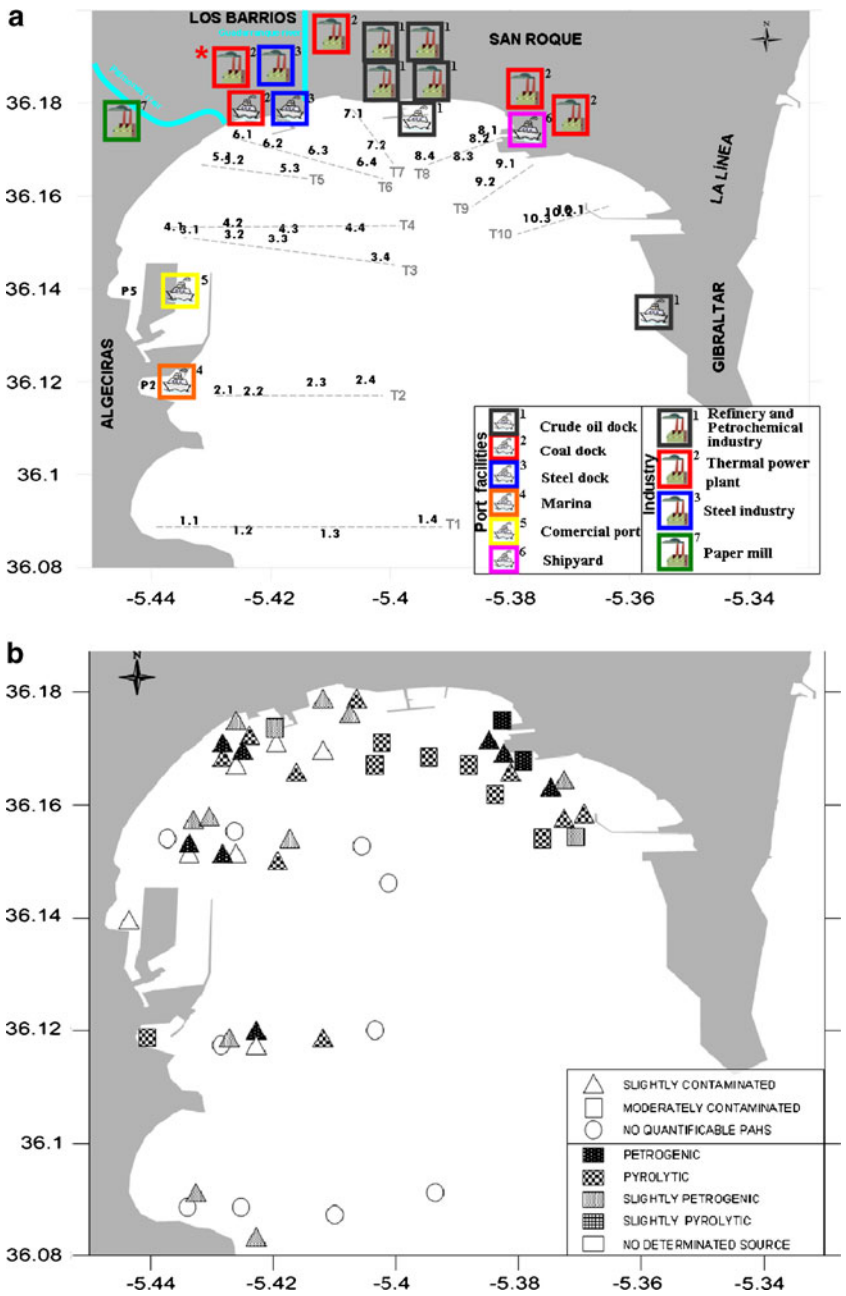

Fig. 1 **a** Sampling area, showing the different sampling points and the most important industries and docks. **b** Sources and levels of polycyclic aromatic hydrocarbons (PAHs) found in the sampling area. * Coal electricity power station, *T* transect

program was: from 50°C (1 min) to 120°C (1 min) at 30°C/min, and from 120°C (1 min) to 260°C (35 min) at 5°C/min. The carrier gas was helium (flow rate 1 mL/min). The capillary column used was DB 1701 (J&W Scientific; http://www.chem.agilent.com). The mass selective detector (MSD) was set to selective ion monitoring (SIM). Retention times and SIM were used for identification. The most abundant ion was used for identification and other ions were additionally used for confirmation. A standard solution containing 16 individual PAHs, in acetonitrile (SUPELCO 47940-u PAH mix) was used for quantification (nine point external standard calibration curve).

Sediment Characterisation

All of the samples were dry-sieved in the laboratory by means of a Ro-Tap machine and seven sieves at 1 phi intervals, obtaining the statistical parameters described by Folk and Ward (1957). Samples with more than 30% fine-grain content (<0.063 mm) were analysed granulometrically using a Galai CIS-1 computerised laser-beam particle analyser. Within this fine-grained content (<0.063 mm), according to Wentworth's classification (Wentworth 1922), the fraction less than 0.002 mm corresponded to clay. As such, a mineralogical analysis was carried out on samples with more than 1% content <0.002 mm. For

Table 1 Levels of PAHs (μg/Kg d.w.), Total Organic Carbon (%) and Depth (m) of sediments. *NAPH* Naphthalene, *ACE* Acenaphthylene, *ACEN* Acenaphthene, *FLUO* Fluorene, *PHE* Phenanthrene, *ANT* Anthracene, *FLUOR* Fluoranthene, *PYR* Pyrene, *B(a)A* Benzo(a)Anthracene, *CHRY* Chrysene, *B(b)F* Benzo(b)Fluoranthene, *B(k)F* Benzo(k)Fluoranthene, *B(a)P* Benzo(a)Pyrene, *B(g.h.i)P* Benzo(g,h,i)Perylene, *DB(a.h)A* Dibenzo(a,h)Anthracene, *I(1.2.3)P* Indeno(1,2,3-cd)Pyrene

M1	1.1.	1.2.	1.3.	1.4.	2.1.	2.2.	2.3.	2.4.	3.1.	3.2.	3.3.	3.4.	4.1.	4.2.	4.3.	4.4.	5.1.	5.2.	5.3.	6.1.	6.2.	6.3.	6.4.	7.1.	7.2.	8.1.	8.2.	8.3.	8.4.	9.1.	9.2.	10.1.	10.2.	10.3.	P.2.	P.5.
NAPH	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	26.7	-	-	-	-	-	13.1	25.6	-	-	20	-	50.1	-	-	-
ACE	-	- [a]	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	37.4	-	-	-	-	-
ACEN	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	400 [b]	-	-	-	-	-
FLUO	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	39.6 [b]	42.3 [b]	-	-	61.4 [b]	-	46.1 [b]	-	-	-
PHE	-	-	-	-	-	40.6	56.8	-	49.1	61.2	193.5	-	-	-	-	-	67.5	122.3	35.9	114.3	61.8	-	161.4	55.3	179.6	-	60.6	123.3	42.3	77.9	295.2 [b]	72.1	145.7	245.8	100.1	-
ANT	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	832[b]	-	-	-	-	75.9	-	-	54.5	-	-
FLUOR	-	-	-	-	-	-	156	-	-	-	321	-	-	-	99.2	-	95.7	-	78.7	155	63.8	-	386	52.7	261	77.2	52.6	279	196	182	435	137	188	680 [b]	211	-
PYR	-	-	-	-	-	-	173	-	94.3	-	340	-	-	-	140	-	125	225	98.2	218	100	-	465	73.6	286	89.8	-	289	222	203	512	162	251	851 [b]	291	-
B(a)A	-	-	-	-	-	-	81	-	-	-	142	-	-	-	-	-	58.5	-	53.5	-	-	-	256	-	135	-	-	186	116	112	379 [b]	76.3	112	315	165	62.1
CHRY	-	-	-	-	-	-	69.4	-	-	-	138	-	-	-	-	-	57.9	-	55.7	-	-	-	286	43.6	140	-	-	191	113	109	360	79.5	115	485 [b]	157	-
B(b)F	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	164	-	79.5	108	-	106	72.4	55.1	160	-	60.8	331	109	-
B(k)F	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	693	-	411	-	-	385	318	317	374	-	-	769	574	-
B(a)P	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	172	-	-	-	-	107	77.6	-	201	-	-	363	126	-
B(g.h.i)P	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	71.5	53.5	-	123	-	-	279	-	-
DB(a.h)A	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
I(1.2.3)P	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	89.3	64.7	-	164	-	-	323	-	-
Σ16 PAH	-	-	-	-	-	41	536	-	143	61	1134	-	-	-	239	-	405	347	322	487	252	-	2583	225	1492	1107	166	1895	1276	1056	3598	527	969	4696	1733	62
Σ10 PAH	-	-	-	-	-	41	363	-	49	61	794	-	-	-	99	-	280	122	224	269	152	-	1954	152	1127	909	126	1458	981	798	2427	365	611	3514	1333	62
TOC	0.0	1.6	0.5	1.0	0.8	0.4	0.8	0.7	0.3	0.6	1.3	0.4	2.5	0.2	1.0	1.0	2.0	2.4	1.3	2.8	1.4	1.8	2.1	0.4	0.8	0.1	0.5	2.5	0.8	0.1	1.1	0.2	0.4	3.4	2.3	2.1
DEPTH	14	32	57	102	17	23	52	84	14	26	53	98	15	24	54	93	16	29	50	15	35	57	111	15	68	25	24	42	69	25	58	10	23	47	3	7

M2	1.1.	1.2.	2.1.	2.2.	3.1.	3.2.	4.1.	4.2.	5.1.	5.2.	6.1.	6.2.	7.1.	7.2.	8.1.	8.2.	9.1.	9.2.	10.2.
NAPH	42.4	25.5	41.5	99.5	139	152	164 [b]	125	132	190 [b]	119	92.9	49.9	38	49.3	35.4	68.5	50.6	66.2
ACE	60.6 [b]	32.9	55.9 [b]	55.5 [b]	48.4 [b]	87 [b]	48.7 [b]	48.4 [b]	57.3 [b]	88.5 [b]	72.8 [b]	118 [b]	-	38.3	45.3 [b]	40.2	92.5 [b]	44.3 [b]	73.8 [b]
ACEN	117 [b]	64.5 [b]	107 [b]	103 [b]	92 [b]	-	93 [b]	91.7 [b]	107 [b]	168 [b]	136 [b]	223 [b]	119 [b]	73.5 [b]	86.1 [b]	75.6 [b]	-	82.3	124 [b]
FLUO	41.8 [b]	22.7 [b]	38.6 [b]	-	33.9 [b]	-	34.2 [b]	33.7 [b]	39.2 [b]	62 [b]	-	83.4 [b]	44 [b]	27.9 [b]	-	-	64.7	-	48.3
PHE	205	74.1	126	120	110	189	118	107	123	197	161	270 [b]	141	93.6	103	89.1	214	101	242
ANT	121 [b]	63.9	108 [b]	108 [b]	94.2 [b]	169 [b]	95.6 [b]	93.4 [b]	108 [b]	171 [b]	141 [b]	232 [b]	122 [b]	75.5	87.9 [b]	-	180 [b]	-	135
FLUOR	43.7	17.1	23.6	16.7	31.9	27.8	79.5	25	24.8	44	35.9	72.2	23.1	31.8	18.4	11.5	76.2	14.5	196
PYR	67.9	30.9	47.3	40.1	49	63.1	83.7	43.4	46.4	77.1	66	115	49	44.5	34.7	27	103	30.6	190
B(a)A	37.5	15.5	22.3	16.9	21.5	26.5	43.4	21.2	20.4	32	32	45.1	19.5	19.4	15.4	10.6	41.3	11.9	74.1
CHRY	15.9	1.67	-	-	1.38	-	27.3	1.28	-	-	3.61	-	-	6.82	-	-	9.41	-	76.1
B(b)F	48.4	22.4	35	31.3	30.8	48.3	42.3	30.8	33.9	52.5	45.7	73.4	35.5	27	26.2	21.3	58.1	23.4	72.9
B(k)F	63.5	30.1	64	44.5	42.8	69.7	56.3	44.1	47.6	74.2	66	102	50.4	37.7	37.3	-	83.7	34.1	97.6
B(a)P	90.5	46.1	76.8	72.4	63	-	80.2	68.1	75.5	118	102	160	82.5	56.2	60.2	-	130	-	125

Table 1 (continued)

M2	1.1.	1.2.	2.1.	2.2.	3.1.	3.2.	4.1.	4.2.	5.1.	5.2.	6.1.	6.2.	7.1.	7.2.	8.1.	8.2.	9.1.	9.2.	10.2.
B(g,h,i)P	113	59.2	96.6	-	-	-	89.9	83.4	-	-	-	-	-	66.9	-	-	-	-	127
DB(a,h) A	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
I(1,2,3) P	73.8	38	59.3	-	-	-	59.5	51.9	56.6	-	76	121	-	42.4	-	-	94.4	-	84
Σ16 PAH	1142	545	902	708	758	832	1116	868	872	1274	1057	1708	736	680	564	311	1216	393	1732
Σ10 PAH	806	371	618	478	504	634	814	620	588	826	737	1095	488	468	372	147	898	212	1223
TOC	0.04	0.14	0.27	0.31	0.94	0.61	0.78	1.37	1.07	2.19	2.25	2.04	1.92	1.55	0.64	2.04	0.71	0.40	1.31
DEPTH	13	21	16	24	14	24	11	19.2	9.5	19	9.6	27.5	11	24.5	14	17	12	18	16

[a] Below determination limit

[b] This amount above ERL (effects range-low)

this, samples were milled in an agate mortar to<40 μm particle size and subsequently analysed by means of a powder X-ray diffraction (XRD) using a Philips PW-1710 diffractometer with automatic slit, Cu$K\alpha$ (http://www.panalytical.com). The presence of clays was determined by the presence of Hilite/Esmectite or Hilite/Moscovite (Table 2).

According to García-Robledo et al. (2008) organic matter was determined by loss on ignition. Carbon content was analysed using a LECO CHNS 932® Analyser (http://www.leco.com). Inorganic carbon was obtained analysing carbon content in samples burned at 550°C for 5 h. The organic fraction (TOC, total organic carbon) was determined as the difference between total (dry sample) and inorganic fractions (burned sample).

Statistical Analysis

Two multivariate techniques were used: principal component analysis (PCA) and cluster analysis. These analyses were carried out with the software Statistica 6.0 (StatSoft®; Tulsa, OK). PCA allowed identification of associations between variables, thus reducing the dimensionality of the data table. This is accomplished by diagonalization of the correlation matrix of the data, which transforms the "*n*" standardised original variables into "*n*" uncorrelated (orthogonal) variables (weighed linear combinations of the original variables) called principal components (PCs). The eigenvalues of the PCs are the measure of their associated variance, the loadings indicate the participation of the original variables in the PCs, and the scores are the name given to the individual transformed observations. A Varimax rotation allows the PCs to be "cleaned up" by increasing the participation of variables with higher contribution, and by simultaneously reducing that of variables with lesser contribution. In that way, the number of original variables contributing to each Varimax rotation is reduced at the cost of a loss of orthogonality.

Cluster analysis is an unsupervised pattern recognition technique that uncovers intrinsic structure or underlying behaviour of a dataset without making a priori assumptions about the data, with the objective of classifying the variables (physical-chemical parameters) or cases (sampling stations) of the system into categories or clusters based on their proximity or similarity. Hierarchical agglomerative cluster analysis was carried out on the standardised data by means of the Wards method of linkage, using Euclidean distances as a measure of similarity (Massart and Kaufman 1983).

Results and Discussion

Occurrence and Levels

Table 1 shows the results obtained for the determination of individual PAHs, as well as the sum of the 16 measured PAHs

and the 10 PAHs required by one of the quality criteria used (Tweede Kamer 1994). Only the compound DB(a,h)A was not detected in any of the samples. With respect to occurrence, during the first sampling campaign (M1) there were points at which no PAHs were detected, whereas in the second campaign (M2) PAHs were detected in every sample. Another clear difference is that very few LPAHs were found during M1, while the presence of practically all 16 PAHs measured in every sample station was observed during M2. This temporal variation might be due to bunkering activities and small spills, which may affect the source of PAHs and increase the level of contamination. Further studies based on sediment sampling over at longer temporal window would give information to ascertain whether the observed variations represent an isolated event or are part of a defined trend. In addition, in the shallow sampling points (< 40 m), the total

Table 2 Granulometry and mineralogy analyses. *Hil* Hilite, *Esm* esmectite, *Mos* Moscovite

Granulometry

Sample	%> 2 mm	2>%> 0.063 mm	%< 0.063 mm	Sample	%> 2 mm	2>%> 0.063 mm	%< 0.063 mm
M1-1.1	1.79	98.03	0.18	M1-8.4	11.52	85.87	2.61
M1-1.2	5.35	91.75	2.9	M1-9.1	6.91	90.89	2.2
M1-1.3	9.32	90.12	0.56	M1-9.2	11.86	84.31	3.83
M1-1.4	5.84	94.03	0.13	M1-10.1	21.3	78.2	0.5
M1-2.1	10.15	89.63	0.22	M1-10.2	4.09	94.79	1.12
M1-2.2	11.48	88.21	0.31	M1-10.3	10.73	88.84	0.43
M1-2.3	8.01	90.84	1.15	M1 P-2	0	0	100
M1-2.4	0	82.32	17.69	M1 P-5	0	0	100
M1-3.1	1.93	97.53	0.54				
M1-3.2	22.34	77.13	0.53	M2-1.1	0.22	99.52	0.26
M1-3.3	0	65.55	34.46	M2-1.2	0.03	99.57	0.4
M1-3.4	5.35	92.11	2.54	M2-2.1	5.09	94.83	0.08
M1-4.1	0	40.58	59.43	M2-2.2	5.62	93.95	0.43
M1-4.2	17.83	81.52	0.65	M2-3.1	6.63	86.92	6.45
M1-4.3	0.02	60.2	39.78	M2-3.2	22.11	76.07	1.82
M1-4.4	0	67.4	32.6	M2-4.1	0.52	89.65	9.83
M1-5.1	0	69.23	30.78	M2-4.2	2.48	89.52	8
M1-5.2	0	54.17	45.84	M2-5.1	0	95.85	4.15
M1-5.3	0	52.97	47.04	M2-5.2	28.91	64.46	6.63
M1-6.1	0	0	100	M2-6.1	1.11	85.31	13.58
M1-6.2	0	0	100	M2-6.2	0.35	90.65	9
M1-6.3	0	0	100	M2-7.1	4.35	88.74	6.91
M1-6.4	0	0	100	M2-7.2	20.31	76.62	3.07
M1-7.1	3.2	94.75	2.05	M2-8.1	24.03	75.09	0.88
M1-7.2	33.95	63.66	2.39	M2-8.2	54.91	44.59	0.5
M1-8.1	6.09	92.8	1.11	M2-9.1	4.63	90.67	4.7
M1-8.2	5.64	91.49	2.87	M2-9.2	8.87	88.45	2.68
M1-8.3	22.32	74.78	2.9	M2-10.2	5.47	93.65	0.88

Mineralogy

Sample	%<0.002 mm	Hil/Esm	Hil/Mos	Σ16 PAH mg / Kg d.w
M1 4.4	0.1	×	××	–
M1 6.1	24.34	×		0.487
M1 6.2	12.55	tr		0.253
M1 6.3	12.86			–
M1 6.4	14.52	×		2.583
M1 P2	13.77	×	×	1.733
M1 P5	12.5	×	×	0.062

concentration of PAHs (Σ16 PAH), was higher in M2. In M1, on the other hand, higher concentrations appeared at deeper points. During M2 it was impossible to take samples at these points.

Where PAH levels were detectable, both low (40.6 μg/kg dw) and high (3,514 μg/kg dw) levels were observed. Other studies carried out in the Bay of Algeciras (Morales-Caselles et al. 2007) found similar results concerning Σ16 PAHs, obtaining values between 1,218 and 1,383 μg/kg dw. These levels of contamination (Σ16 PAHs) are lower than those observed in other ports. For example, in the Port of Barcelona, where concentrations as high as 10,320 μg/kg dry weight have been observed (Martínez-Lladó et al. 2007) or the Port of Santander, where concentrations of up to 9,880 μg/kg dry weight have been detected (Viguri et al. 2007). In surface sediments of Sydney Harbour, concentrations as high as 380,000 μg/Kg dry weight were found (McCready et al. 2000), and in Milwaukee Harbour concentrations around 90,000 μg/kg dry weight were found (Ghosh et al. 2000).

Sediment Quality

In order to evaluate the degree of PAH contamination of the samples, two quality criteria were compared with the levels obtained in the sediments: the ERL (effects range-low) proposed by the National Oceanic and Atmospheric Administration (NOAA 1999), and the Tweede Kamer (1994) criteria. ERL should be understood and used as an estimation of the concentration below which toxicity is improbable. NOAA establishes the ERL for 12 of the 16 PAHs measured in this study. In Table 1, the PAH concentrations above the ERL are indicated. In M1, only 6 of the 36 sites sampled showed concentrations of one or more individual PAH that exceeds the ERL. These samples were located in transects 8, 9 and 10 (8.x., 9.x. and 10.x.). On the other hand, between 1 and 5 PAHs show concentrations above the ERL in all of the sites sampled during M2.

Figure 1b indicates the degree of contamination of each point according to the Tweede Kamer criteria (1994): 34 of the 55 samples can be considered as slightly contaminated, 11 were moderately contaminated, 10 did not present quantifiable levels of PAHs and no site presented PAH levels that would classify it as contaminated or highly contaminated.

Sources of PAHs

Figure 1b indicates levels of pollution of PAHs and the source of these compounds. In order to discern whether the PAHs were from pyrolytic or petrogenic sources, two indicators were used: the ratio between low- and high-molecular weight PAHs, (LPAH/HPAH) (De Luca et al. 2004), and the FLUOR/PYR ratio (Jiang et al. 2007). For both indicators, a value equal to "1" is the limit between pyrolytic and petrogenic sources. As such, values close to 1 (± 0.5) were considered slightly pyrolytic (0.5–1) or slightly petrogenic (1–1.5). Considering the 55 samples, 18% were petrogenic, 29% were pyrolytic, 22% were slightly petrogenic, 0% was slightly pyrolytic and 31% were of undetermined source (absence of LPAH, HPAH, FLUOR or PYR).

Sedimentology and Granulometry

The results of the granulometric and mineralogical analyses are shown in Table 2. Of the 55 samples analysed, 12 show a fraction of fine-grained content (<0.063 mm) higher than 30%. Of these 12 samples, 7 had more than 1% content <0.002 mm. Of these 7 samples, M1_6.1 is the sample with highest content of fine-grain sediment (Table 2). Samples M1_P2, M1_P5 and M1_6.4, had similar percentages of fine-grain content <0.002 mm and clay (Table 2). In third place is the group comprised of M1_6.2 and M1_6.3, with almost no fine-grain content <0.002 mm and no clay

Table 3 Principal component analysis (PCA)

	Factor loadings (Varimax norm)		
	Extraction: principal components		
	(Marked loadings are > 0.700000)		
Variable	Factor 1	Factor 2	Factor 3
%>2 mm	*	*	*
% (0.063 – 2 mm)	*	*	0.903674
%<0.063 mm	*	*	-0.933824
% TOC	*	*	-0.752233
Naphthalene	*	0.839012	*
Acenaphthylene	*	0.935218	*
Acenaphthene	*	0.812483	*
Phenanthrene	*	0.897909	*
Fluorene	*	0.835089	*
Anthracene	*	0.653582	*
Fluoranthene	0.959330	*	*
Pyrene	0.949925	*	*
Benzo(a)Anthracene	0.930078	*	*
Chrysene	0.968535	*	*
Indeno(1,2,3-cd)Pyrene	0.614651	0.612661	*
Benzo(b)Fluoranthene	0.736654	0.556595	*
Benzo(k)Fluoranthene	0.858884	*	*
Benzo(a)Pyrene	0.514750	0.800626	*
Benzo(g,h,i)Perylene	0.546374	*	*
Eigenvalue	8.244246	4.006555	2.145224
% Total variance	43.39077	21.08713	11.29065
Cumulative Eigenvalue	8.24425	8.24425	14.39603

*Below 0.5

(Table 2). Last, sample M1_4.4 is the sample with the least fine-grain content (two orders of magnitude lower).

Generically, the samples with the highest potential for absorption would be those with higher fine content <0.002 mm and a higher content of clay. In other words, the samples with the highest potential for absorption would be M1_6.2, M1_P2 and M1_P5. However, this does not correspond with the PAH levels observed in these samples (Table 1). For example, comparing M1_P2 with M1_P5, which have similar fine content <0.002 mm and clay content (Table 2), there is a difference of two orders of magnitude in PAH content (Table 1). Furthermore, it can be

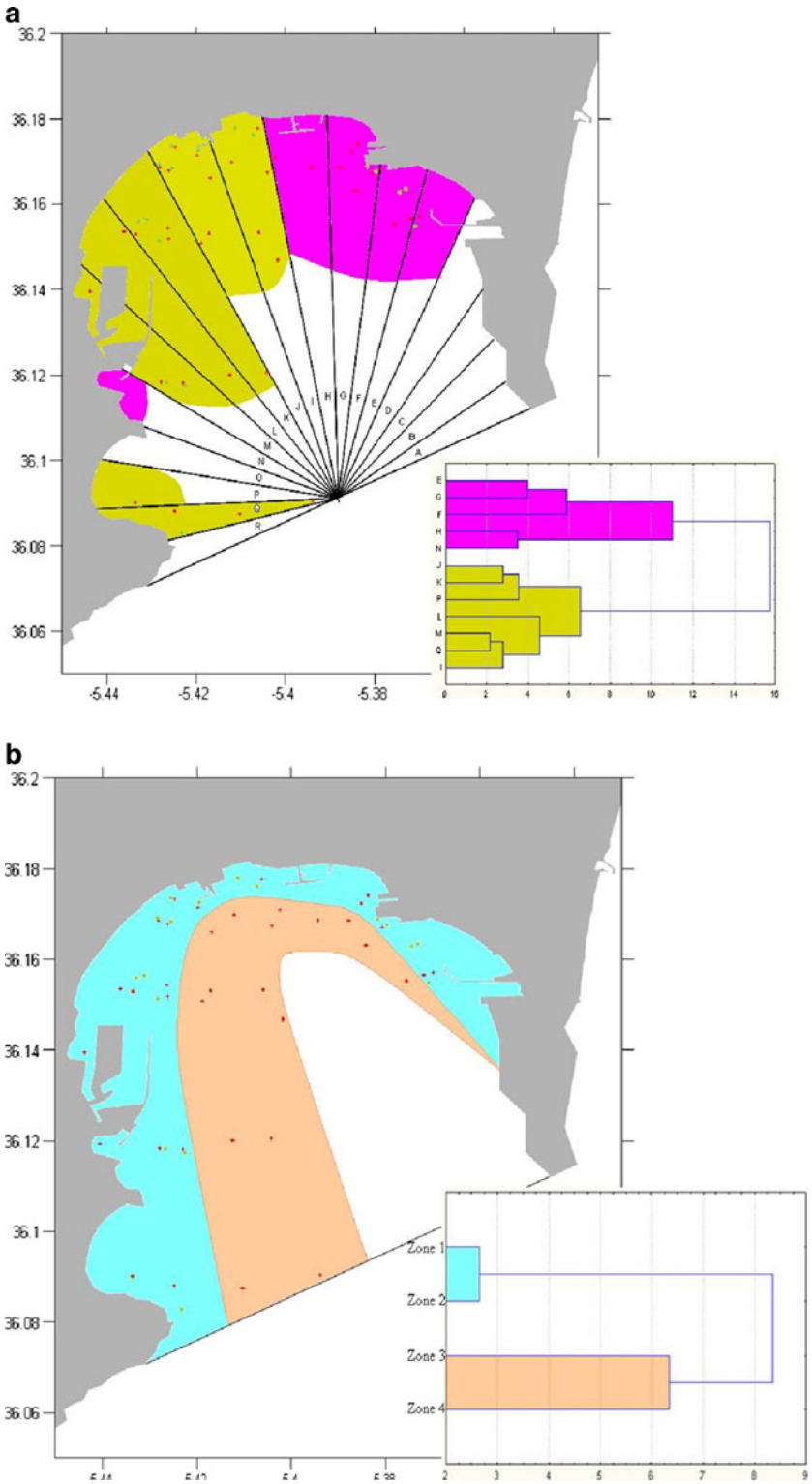

Fig. 2 **a** Cluster depending on depth and its representation in the study area. **b** Cluster depending on spatial location and its representation in the study area

observed that sites with completely different granulometry show similar levels of contamination (for example M1_6.2 and M1_7.1). These results show that there is no relation between the granulometry/mineralogy of the sediments and the levels of PAHs. These levels are related more strongly to the spatial location of the sampling points.

Spatial Distribution

Factorial analysis with extraction of PCs was used to establish patterns of spatial distribution of PAHs in this work. The results are shown in Table 3. Factors 1#, 2# and 3# account for 75.7% of the total variance of the dataset. Factor 1# (43.4 % variance) is directly related to 6 of the 10 high-molecular weight PAHs (HPAH). Factor 2# (21.1% variance) is related to 5 of the 6 LPAHs. Factor 3# (11.3% variance) corresponds with the sediment characteristics (granulometry and TOC). The first two factors are clearly related to the pollutants analysed (PAHs), and together they account for 64.5% of the total variance. Furthermore, each group of PAHs (high- and low-molecular weight) has its own characteristics as far as source is concerned, with some being associated with pyrolytic sources (HPAH) and others associated with petrogenic sources (LPAH) (De Luca et al. 2004), and each one is grouped under one factor.

Cluster analysis allowed zoning of the bay according to the PAH concentration in sediments. A first cluster analysis (Fig. 2a) was carried out using the components of the two factors of factorial analysis (i.e. each PAH) plus location depth. The sampled sites were classified under four bathymetric zones: Zone 1 (0 – 20 m), Zone 2 (20 – 40 m), Zone 3 (40 – 80 m) and Zone 4 (>80 m). Fig. 2a shows how bathymetric zones 1 and 2 are highly related and form a group [blue area on the map (in print version light grey)]. Similarly, zones 3 and 4 form another group [light orange area (in print version dark grey)]. A second cluster analysis (Fig. 2b) was carried out in order to establish whether, apart from depth, the spatial location of the points was a determining factor concerning levels and types of PAHs in the sediment. Thus, the bay was divided into regions of 10 degrees, identified in alphabetical order, counterclockwise (Fig. 2b). For this second cluster analysis, the variables selected were those grouped in factor 1# and 2# of the factorial analysis and the spatial localisation of the sampling points. Two clearly differentiated groups [one in pink and the other in yellow (in print version one in dark grey and the other in light grey)] can be seen in Fig. 2b.

According to the results obtained in the cluster depending on depth and in the cluster depending on spatial location, the bay was divided into 5 zones, as shown in Fig. 3.

- Zone 1: Area in the north-eastern part of the bay corresponding to the deepest sampled areas. This zone is moderately contaminated by PAHs from pyrolytic sources. In this zone, the source of PAHs is probably linked to industrial activities (i.e. the coal electricity power station and/or the nearby petrochemical plants (see Fig. 1a).
- Zone 2: Area in the north-eastern part of the bay, close to the coast, where slight to moderate PAH contaminated sediments from petrogenic sources predominates. This may be due to the activities of the refinery docks (Fig. 1a) or small spills that reach the coast from the various ships operating in the bay.
- Zone 3: The Port of El Saladillo, which has moderate contamination linked to pyrolytic PAH sources. The source could be related to urban runoff processes (Brown and Peake 2006) which supply a watercourse flowing from the city of Algeciras into the Bay, close to the sampling point P2.
- Zone 4: Area in the western arch of the Bay that corresponds to the deepest part of the arch, where contamination oscillates between slight and unquantifiable.
- Zone 5: The shallowest part of the western region. This zone is slightly contaminated by pollutants of mainly petrogenic and undetermined sources.

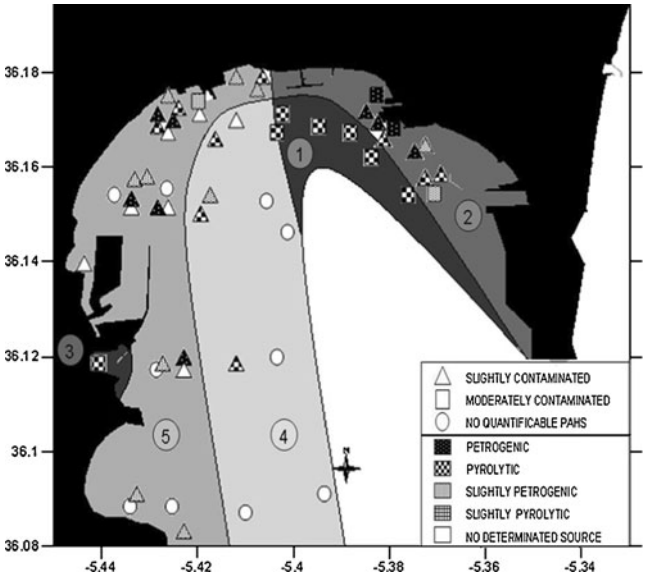

Fig. 3 Zoning obtained using the results of the cluster depending on depth, and the cluster depending on the spatial location

Conclusions

New spatial distribution analysis methodology proposed in this work for the study of the sediments of semi-enclosed bodies of water, together with factorial analysis and cluster analysis, provide a very useful tool for the study of marine sediment pollution. These instruments have proven to be adequate to define different areas according to levels and

sources of PAHs in the sediments. This zoning allows establishment of priority areas in order to develop programs to improve the environmental quality of the sediments in this Bay. This methodology of zoning using multivariate analysis tools can be extrapolated to other environmental areas. The sediments studied in the Bay of Algeciras are slightly-to-moderately contaminated by PAHs. The source of PAHs in the Bay is equally pyrolytic and petrogenic. In this Bay there is no relation between the granulometry/mineralogy of the sediments and the levels of PAHs. The levels of PAHs are related more strongly to the spatial distribution of the gathered samples. In the study area, the concentration of PAHs increases as depth increases, which shows the importance of deeper sediment characterisation.

Acknowledgements The work described was supported partly by the projects OT 2006/048 and P06-FQM-02075 financed by the Regional Government, Junta de Andalucia (Spain). E.R.-N. thanks the Obra Social la Caixa for funding her master's grant, and she thanks the Ministry of Science and Innovation for funding her research fellowship (FPU). We are grateful for the collaboration of the doctors Giuseppe Cultrone and Daniel Gonzalez-Fernandez. We would like to thank the University Cadiz School of Modern Languages (CSLM) and Mrs Denise Hughes for English correction.

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